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ABSTRACT

This report describes the technical progress made on the Pittsburgh Air Quality Study (PAQS) during the period of March 2003 through August 2003. Significant progress was made this project period on the source characterization, source apportionment, and deterministic modeling activities. Major accomplishments included: Development of an emission profile for an integrated coke production facility and simulations using PMCAMx for a two week period during July 2001. The emissions from the coke facility are dominated by carbonaceous compounds. Forty seven percent of the organic carbon mass was identified on a compound level basis. Polycyclic aromatic hydrocarbons were the dominant organic compound class in the coke emissions. Initial comparisons with the data collected in Pittsburgh suggest good agreement between the model predictions and observations. Single particle composition data appear useful for identifying primary sources. An example of this unique approach is illustrated using the Fe and Ce particle class with appear associated with steel production.

TABLE OF CONTENTS

Disclaimer	2
Abstract	3
Table of Contents	4
List of Figures	5
Introduction	6
Introduction	6
Experimental	6
Activity 1. Project Management	6
Activity 2. Ambient Monitoring	7
Activity 3. Source Characterization	7
Activity 4. Source Apportionment	10
Activity 5. Three-Dimensional Deterministic Modeling	11
Results and Discussion	14
Pittsburgh Air Quality Study Overview and Initial Scientific Findings	14
Modeling the diurnal variation of nitrate during the Pittsburgh Air Quality Study	15
Ambient Aerosol Size Distributions and Number Concentrations Measured During the Pittsburgh Air Quality Study (PAQS)	15
Spatial Variations of PM _{2.5} During the Pittsburgh Air Quality Study	15
Light scattering by fine particles during PAQS: Measurements and modeling	16
Meteorological influence on, and patterns in ambient fine particulate chemical composition at two sampling sites in metropolitan Pittsburgh: A 2001 intensive summer study.	17
Mass size distributions and size resolved chemical composition of fine particulate matter at the Pittsburgh Supersite	17
Semi-Continuous PM _{2.5} Inorganic Composition Measurements During The Pittsburgh Air Quality Study	18
Mass Balance Closure and the Federal Reference Method for PM _{2.5} in Pittsburgh, Pennsylvania	18
Ambient Measurements of Metal-Containing PM 2.5 in an Urban Environment Using Laser-Induced Breakdown Spectroscopy	19
Conclusions	20
Presentations and Publications	20
Publications:	20
Presentations:	22

LIST OF FIGURES

Figure 1. Composition of organic particulate matter emitted from coke production facility.	8
Figure 2. Distribution of OC/EC and trace metals emitted from large integrated coke production facility. Figure compares profiles developed for four different periods..	9
Figure 3. Characteristic mass spectrum of the iron (Fe) and cerium (Ce) particles measured by the UC Davis single particle mass spectrometer.	11
Figure 4. Frequency of the observations of the iron/cerium particles as a function of wind direction in the Pittsburgh Supersite.	11
Figure 5. Predicted PM _{2.5} sulfate by PMCAMx+ during July 17, 2001 (daily average). This day represents the peak of that air pollution episode in Pittsburgh.	13
Figure 6. Predicted (red line) and observed (blue symbols) PM _{2.5} and PM _{2.5} sulfate concentrations in Pittsburgh for the first seven days of the simulation (July 12-18. 2001).	13
Figure 7. Predicted (red line) and observed (blue symbols) PM _{2.5} organic matter (OM) and PM _{2.5} EC concentrations in Pittsburgh for the first seven days of the simulation (July 12-18. 2001).	14

INTRODUCTION

This is the fifth semi-annual report of the “Pittsburgh Air Quality Project” (PAQS) funded by the U.S. Department of Energy’s National Energy Technology Laboratory under DOE Cooperative Agreement No. DE-FC26-01NT41017 to Carnegie Mellon University. This research is also supported by the US EPA through the Supersites program. In this three-year project, Carnegie Mellon University will conduct detailed studies of the ambient particulate matter in the Pittsburgh, PA metropolitan area. The work includes ambient monitoring, source characterization, and modeling (statistical and deterministic) for source apportionment. The major objectives of the project include:

- To achieve advanced characterization of the PM in the Pittsburgh region. Measurements include the PM size, surface, volume, and mass distribution; chemical composition as a function of size and on a single particle basis; temporal and spatial variability.
- To obtain accurate current fingerprints of the major primary PM sources in the Pittsburgh region using traditional filter-based sampling and state-of-the-art techniques such as dilution sampling and single particle analysis using mass spectroscopy and LIBS.
- To estimate the impact of the various sources (transportation, power plants, natural, etc.) on the PM concentrations in the area using both statistical and deterministic models.
- To quantify the responses of the PM characteristics to changes in these emissions in support of the emission control decision making in the area.
- To develop and evaluate current and next generation aerosol monitoring techniques for both regulatory applications and for determination of source-receptor relationships.

EXPERIMENTAL

This section provides an overview of the effort on various project activities. This project period the majority of the effort went into Activity 3 Source Characterization, Activity 4 Source Apportionment, and Activity 5 Three-Dimensional Modeling.

Activity 1. Project Management

During this project period a data analysis meeting was held in Pittsburgh in conjunction with the PM2003 Conference. The workshop consisted of two half day sessions during which PAQS project team members described the status of the research and future plans.

Substantial progress was made this project period finalizing the ambient data set and implementing into the NARSTO. The format of fifteen of the 31 datasets has been approved by NARSTO, and another five are close behind. We will continue to work on

finalizing the data format. We have transferred the data for which the format has been certified to Clarkson University for inclusion in EPA sponsored the relational database, and to Advanced Technology Systems for inclusion in the DOE sponsored web-base database.

The QA/QC report for the ambient sampling has been submitted to EPA.

Activity 2. Ambient Monitoring

The purpose of this activity is to create an extensive database of ambient PM measurements for source apportionment, examination of aerosol processes, evaluation of instrumentation, and air quality model development and evaluation. The ambient sampling phase of the Pittsburgh Air Quality Study was successfully completed at the end of September 2002. Approximately sixteen months of data were collected, including three intensive sampling periods (July 2001, January 2002, and July 2002) and several special experiments (instrument intercomparison, nucleation, etc). The structure in Schenley Park has been removed and the site restored to its original conditions per our agreement with the City of Pittsburgh.

We made significant progress this project period finishing up the analysis of the archived samples collected during the ambient monitoring. Notable milestones achieved this project period included Florida Internal University (supported by the EPA part of the project) completing the extraction and GC-MS analysis of the samples collected for organic speciation. Carnegie Mellon University finalized the extraction and analysis procedures for the metal samples; nine months of PM₁₀ and PM_{2.5} data are now available for 22 elements via ICP-MS. We expect to finish analyzing the remaining ambient metals samples sometime during the next project period. Rutgers University completed the FTIR analysis of organic functional groups and has begun performing the organic polar fraction analysis. The analysis of archived ambient samples should be completed sometime in Winter of 2004 resulting in a sixteen month data set of daily or higher frequency measurements of a large number of PM parameters.

Activity 3. Source Characterization

Many primary sources of atmospheric aerosols for the Pittsburgh region are inadequately characterized. The purpose of this activity is to develop updated emission profiles for important source categories around Pittsburgh.

Major progress was made this project period analyzing the fence line data collected adjacent to a large coke production facility. Combining the fence line site, background site, and meteorology data we have developed an integrated emission profile for the coke facility. The profile includes 45 individual organic species that make up about 47% of the organic particulate mass. The organic particulate emissions from the coke facility emissions are dominated by PAH. This profile developed from the organic speciation data is shown in Figure 1. The profile also contains organic and elemental carbon

(OC/EC), as well as a number of metals measured using the high time resolution samples collected by the University of Maryland. The profile of metals and OC/EC for several different sampling periods is summarized in Figure 2. This new profile is now being used in the statistical source receptor modeling of the ambient data.

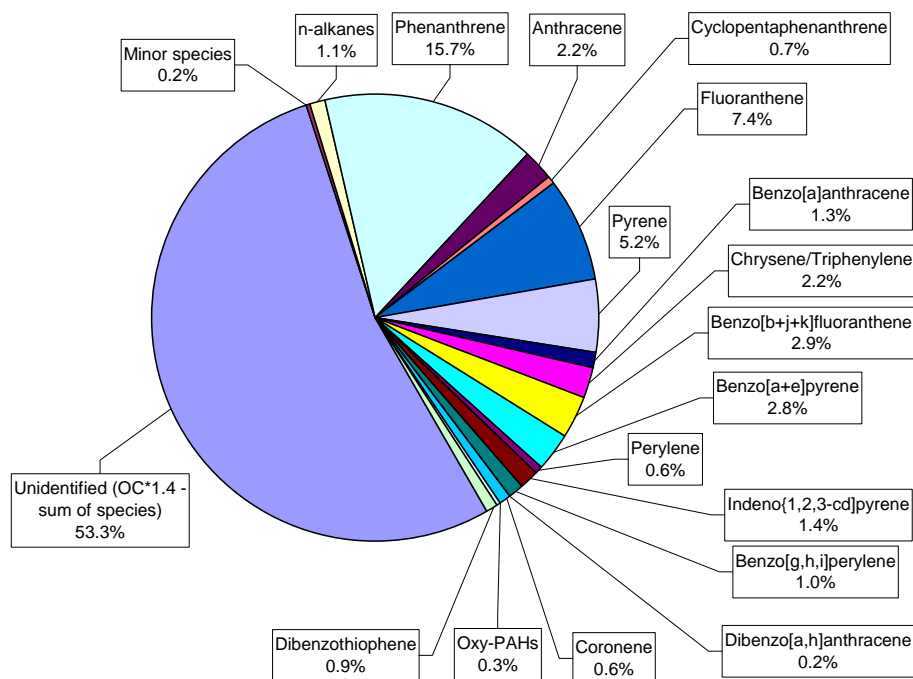


Figure 1. Composition of organic particulate matter emitted from coke production facility.

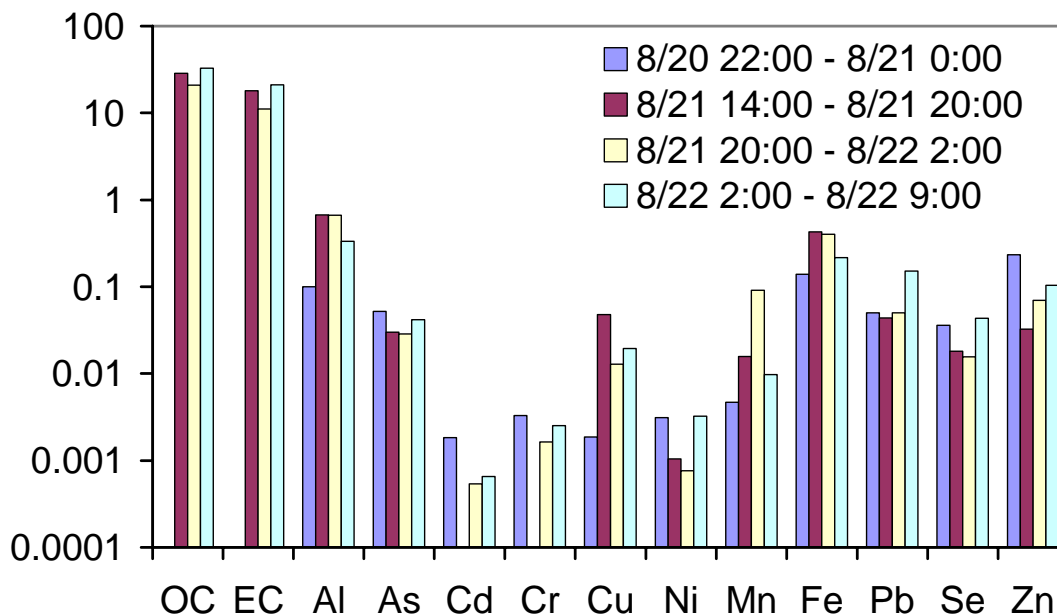


Figure 2. Distribution of OC/EC and trace metals emitted from large integrated coke production facility. Figure compares profiles developed for four different periods.

Progress was also made this project period analyzing the data from the highway tunnel experiment. The goal of this experiment was to develop an emission profile for in use vehicles in the Pittsburgh area. The analysis of the air quality data collected in the tunnel this project period focused on performing quality assurance and quality controls checks and corrections for background levels. We hope to use the tunnel data to develop emission profiles for both gasoline and diesel vehicles using correlations of the air quality data with information on vehicle class and vehicle operating conditions. We worked on obtaining this traffic data through the analysis the videotapes for traffic flow. Finally, after much negotiation with the Federal Highway Administration and Mobility Technologies we also have a copy of the electronic data collected by the on road sensors on I-376. The data set is now complete and ready for final analysis to develop emission profiles and emission rates for mobile sources in the Pittsburgh region.

A second scoping investigation was performed this project period at the Allegheny County Health Department North Braddock monitoring site to evaluate the feasibility of fence line sampling for the steel facility. The original scoping study found insufficient $PM_{2.5}$ signal above background for fence line sampling. For the second scoping study we measured wind speed and direction, SO_2 and total particle number concentrations. The results suggest that the plume from the facility intermittently hits the sampling site. We are currently considering going back to the site with the University of Maryland SEAS sampler to investigate the metals emissions from the facility, in particular Se.

We developed a system to resuspend road dust and other material in a Teflon bag in order to collect $PM_{2.5}$ samples for chemical speciation. Using this system we

resuspended and collected PM_{2.5} road dust samples onto filters for chemical analysis. We also collected a resuspended leaf detritus samples this project period for chemical analysis. Two road dust samples were collected: one for an urban road and one for a rural road. The samples are currently waiting analysis.

Significant effort was expended this project period to identify a full-sized coal fired power plant for characterization. Working with DOE, NESCAUM, and the Carnegie Mellon Carnegie Mellon University Electricity Center we have contacted PSEG, First Energy, Southern Company, and TVA about characterizing one of their facilities. To date, no one is willing to grant us access to one of their facilities.

Activity 4. Source Apportionment

Groups at Clarkson University, University of California Davis, Brigham Young University, and Carnegie Mellon University conducted significant work to apportion the sources of fine particulate matter in the Pittsburgh area this project period. Work at Clarkson University focused on development of a factor analysis model that will permit us to utilize data obtained at different sampling frequencies so we do not lose the information contained in the shorter-term values by averaging them back to the longest interval sample. Researchers at Clarkson also continued to work on apportioning particle size distributions extending their previous work which just examined data for the July 2001 period to the entire year. The Clarkson University team is currently performing source attribution combining daily average metal concentrations and 15 minute concentration measurements collected by the SEAS instrument of the University of Maryland (Ondov). This new approach allows the traditional analysis to take advantage of the high temporal resolution of the SEAS measurements. The resulting model permits the extraction of source information on the same time scale as the data were obtained and thus should provide close to optimum source identification and resolution.

By combining single particle composition and meteorology data researchers at the University of California have been able to correlate particle classes to individual stationary sources in the Pittsburgh region. An example of this unique approach is illustrated below. One of the classes of particles identified in the ambient atmosphere of Pittsburgh by the RSMS-III had characteristic peaks of iron and cerium (Figure 3). These particles appeared almost exclusively when the wind direction was between 135° and 160° (Figure 4). There are two steel mills roughly 10 miles from the site located at 137° and 163°. Please note that the contributions of the steel mills to the measured PM_{2.5} were less than 1% by mass, demonstrating the power of this new technique.

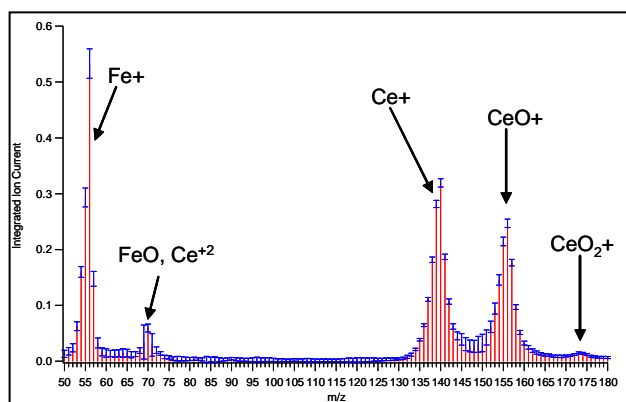


Figure 3. Characteristic mass spectrum of the iron (Fe) and cerium (Ce) particles measured by the UC Davis single particle mass spectrometer.

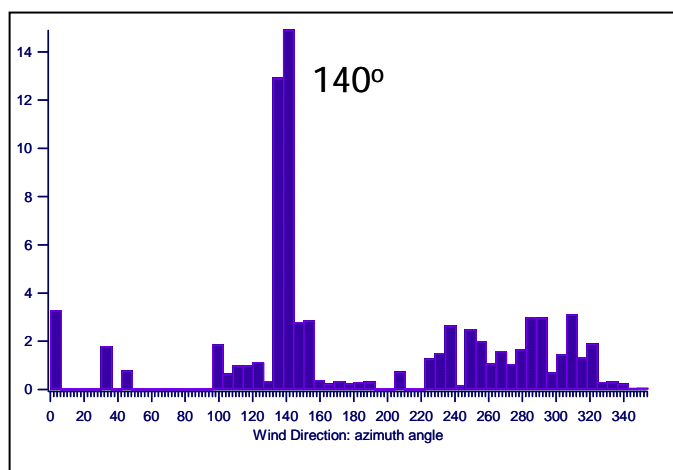


Figure 4. Frequency of the observations of the iron/cerium particles as a function of wind direction in the Pittsburgh Supersite.

Researchers at Brigham Young University focused on using UNMIX and PMF to compare sources of semi-volatile organic material at the Schenly Park Supersite and the NETL Pittsburgh campus. Finally, researchers at Carnegie Mellon have focused on using CMB and molecular tracers to apportion the organic aerosol, and UNMIX to apportion sources of trace elements.

Activity 5. Three-Dimensional Deterministic Modeling

The Comprehensive Air quality Model with extensions (PMCAMx) is a publicly available computer modeling system for the integrated assessment of photochemical and PM pollution. This CTM has been recently upgraded by the CMU team and ENVIRON to include state-of-the-art description of aerosol dynamics and thermodynamics, cloud chemistry, and wet removal processes. PMCAMx+ is the research version of the code and it includes the latest developments in Carnegie Mellon organic and inorganic aerosol and

aqueous-phase chemistry modules. The aerosol module has flexible size resolution and includes three different descriptions of aerosol dynamics (equilibrium, hybrid, and dynamics). A different sub-module can be used for each computational cell for each timestep based on the timescale for equilibrium in this cell, the acidity differences among particles of different sizes, or the location of the cell. For example, the simplest and fastest approach is used for the cells far from the area of interest. A similar flexible approach is used by the Variable Size Resolution Model (VSRM) for cloud chemistry. These tools are as accurate as the descriptions used by other CTMs but are faster by one to two orders of magnitude.

During this project period we focused on simulating the second half of the July 2001 Eastern Supersites Intensive (July 12-July 28, 2001) to evaluate the ability of the model to reproduce the observations. Emission inventories were developed in collaboration with LADCO. As discussed below the results from this initial comparison are encouraging. We are currently collecting the data from the other Eastern Supersites and the rest of the PM measurement networks to extend the evaluation to areas other than Pittsburgh and Western Pennsylvania.

After the evaluation of the modeling tool, we will use it to investigate the source-receptor relationships in the Eastern US and to synthesize the measurements of the Pittsburgh Supersite. Examples include investigations of the response of the system to SO₂ emission controls and the potential for increase in nitrate, the role of ammonia in the formation of ammonia nitrate, the responses of the PM to changes in NO_x and VOC emissions, the relative role of primary and secondary organic aerosol, the identification of the major precursors of secondary organic aerosol, etc.

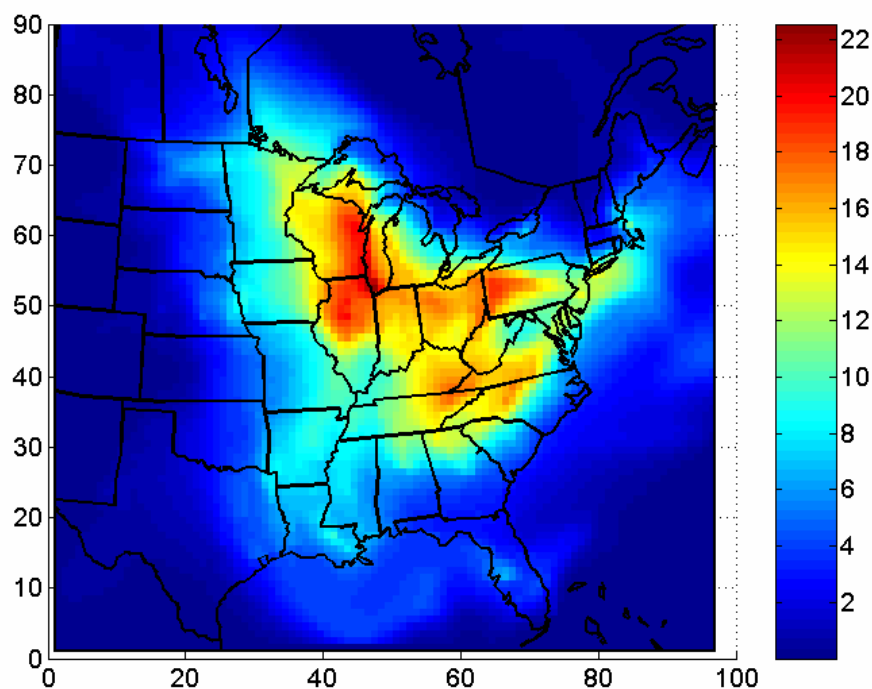


Figure 5. Predicted $\text{PM}_{2.5}$ sulfate by PMCAMx+ during July 17, 2001 (daily average). This day represents the peak of that air pollution episode in Pittsburgh.

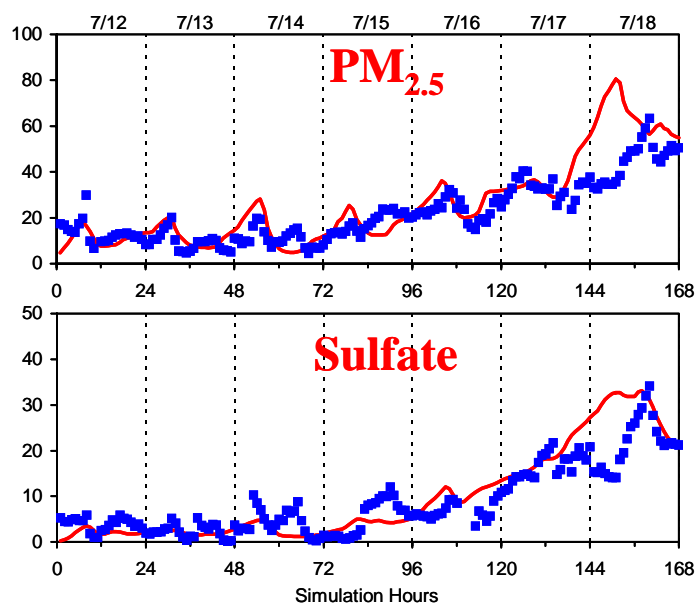


Figure 6. Predicted (red line) and observed (blue symbols) $\text{PM}_{2.5}$ and $\text{PM}_{2.5}$ sulfate concentrations in Pittsburgh for the first seven days of the simulation (July 12-18, 2001).

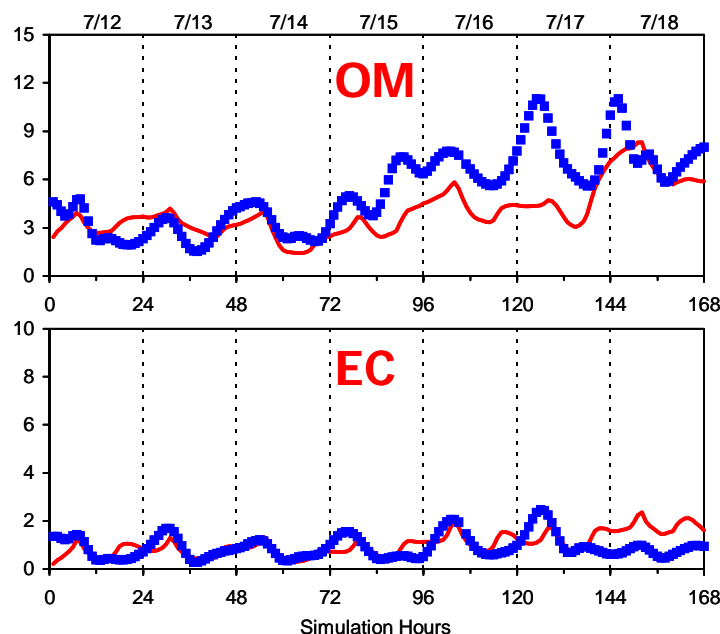


Figure 7. Predicted (red line) and observed (blue symbols) PM_{2.5} organic matter (OM) and PM_{2.5} EC concentrations in Pittsburgh for the first seven days of the simulation (July 12-18, 2001).

RESULTS AND DISCUSSION

The main findings of the PAQS papers submitted for publication during the report period are summarized below.

Pittsburgh Air Quality Study Overview and Initial Scientific Findings

Ambient sampling for the Pittsburgh Air Quality Study (PAQS) was conducted from July 2001 to September 2002. The study was designed (1) to characterize particulate matter (PM) by examination of size, surface area, and volume distribution, chemical composition as a function of size and on a single particle basis, morphology, and temporal and spatial variability in the Pittsburgh region; (2) to quantify the impact of the various sources (transportation, power plants, biogenic sources, etc.) to the aerosol concentrations in the area; and (3) to develop and evaluate the next generation of atmospheric aerosol monitoring and modeling techniques. Recent findings of PAQS obtain closure of the Pittsburgh aerosol mass balance if water is included; recommend methods to obtain accurate high time resolution organic material and PM_{2.5} nitrate, sulfate, and mass measurements; estimate the portion of the Pittsburgh organic carbon concentrations that are secondary in origin; describe the diurnal variations in aerosol sulfate and the partitioning of nitrate between the aerosol and gas phases; and quantify the impact of fine particle generation by nucleation. Monthly average and diurnal patterns in aerosol number concentration, and aerosol nitrate, sulfate, elemental carbon,

and organic carbon concentrations, light scattering as well as gas-phase ozone, nitrogen oxides, and carbon monoxide are discussed with emphasis on the processes affecting them. (Wittig et al. Submitted to Atmospheric Environment)

Modeling the diurnal variation of nitrate during the Pittsburgh Air Quality Study

A thermodynamic model, GFEMN, was used to simulate the partitioning of nitrate aerosol and nitric acid using highly time-resolved inorganic measurements collected at the Pittsburgh Air Quality Study during July 2001 and January 2002. Model results were evaluated using independent, high time-resolution measurements of aerosol nitrate. The mean observed concentration in July was 0.6 $\mu\text{g}/\text{m}^3$ and 2.1 $\mu\text{g}/\text{m}^3$ in January. Model predictions were in agreement with the observations within 0.5 $\mu\text{g}/\text{m}^3$ on average, with measurement uncertainties often accounting for these discrepancies. The simulations were run assuming particles were liquid in July for all relative humidities (RHs) and solid below 60% RH in January. For both seasons the assumed physical state did not influence considerably the overall agreement with observations. The assumption of particle mixing state did appear to influence model error, however- assuming that particles were externally mixed during low RH periods in July improved agreement significantly. The exceptional sensitivity of predicted aerosol nitrate to ammonia in Western Pennsylvania suggests that reductions in PM_{2.5} may be assisted by reductions in ammonia emissions. (Takahama et al., Submitted to Atmospheric Environment)

Ambient Aerosol Size Distributions and Number Concentrations Measured During the Pittsburgh Air Quality Study (PAQS)

Twelve months of aerosol size distributions from 3 nm – 560 nm, measured using Scanning Mobility Particle Sizers (SMPS) are presented with an emphasis on average number, surface, and volume distributions, and seasonal and diurnal variation. The measurements were made at the main sampling site of the Pittsburgh Air Quality Study from July 2001 – June 2002. These are supplemented with 5 months of size distribution data from 0.5-2.5 μm measured with a TSI Aerosol Particle Sizer (APS) and 2 months of size distributions measured at an upwind rural sampling site. Measurements at the main site were made continuously under both low and ambient relative humidity. The average Pittsburgh number concentration (3-500 nm) is 22,000 cm^{-3} with an average mode size of 40 nm. Strong diurnal patterns in number concentrations are evident as a direct effect of the sources of particles (atmospheric nucleation, traffic, and other combustion sources). Nucleation (involving sulfuric acid) is active on the 30-50% of study days and over a wide area (at least a hundred kilometers). Rural number concentrations are a factor of 2-3 lower (on average) than the urban values. Average measured distributions are different than model literature urban and rural size distributions. (Stanier et al. Submitted to Atmospheric Environment)

Spatial Variations of PM_{2.5} During the Pittsburgh Air Quality Study

Measurements of 24-hour PM_{2.5} total mass, sulfate, ammonium, and organic carbon show similar concentrations within experimental error at six sampling locations separated by

more than 300 km. The measurements were obtained during summer 2001 in the center of Pittsburgh as well as in less populated areas upwind and downwind of the city. Measurable differences among the six sites were observed for nitrate and elemental carbon during the same time period. In contrast, measurable differences were observed for total mass and all five chemical species at the same sites during winter 2002. The results suggest that concentrations may be remarkably uniform over large areas due to secondary aerosol production from gases emitted in upwind areas. Air mass trajectory calculations show that concentrations can steadily increase along a trajectory, and that regions downwind of a city such as Pittsburgh are affected by city emissions; however, $PM_{2.5}$ levels measured within the city may not be significantly affected by local emissions if background levels are sufficiently high. (Tang et al. Submitted to Aerosol Science & Technology)

Light scattering by fine particles during PAQS: Measurements and modeling

Light scattering by fine particulate matter was measured at the Pittsburgh Air Quality Study (PAQS) using an Optec NGN-3 nephelometer during the summer 2001 (July and August) and the winter 2002 (January). Scattering coefficient measurements were performed as close to ambient conditions as possible. Several approaches are used for the theoretical calculation of scattering coefficient and the results are compared to the direct measurements to identify the principal causes contributing to visibility degradation during PAQS. The first approach uses ambient high-time and daily resolved $PM_{2.5}$ composition concentrations to estimate the scattering coefficient assuming that the aerosol is an external mixture. The second approach uses a thermodynamic model and Mie theory to predict the scattering coefficient of aerosols from daily size-composition distributions. The third approach introduces high-time and daily resolved ambient aerosol water concentrations and concentrations of sulfate, nitrate, organic material and soil with fixed scattering efficiencies.

During the summer the first two approaches underestimate the measured scattering coefficient by around 20%. Good agreement is obtained between the measured scattering coefficient and the model incorporating measured water aerosol concentrations. The failure of the thermodynamic model to accurately reproduce the scattering coefficient might be an indication that the organic compounds are contributing to aerosol water uptake under certain conditions. During the winter the first two approaches tend to over-predict the measured scattering by around 15%. This over-prediction is weakly correlated to the organic mass. The organic mass conversion factor from organic carbon measurements might be too high for the winter aerosol. Sulfate, and the associated water, contributes around 70% to the scattering coefficient during the summer. Organic material contributes 30% of the scattering coefficient during the summer. During the winter, sulfate accounts for around 40%, nitrate around 30% and organic material around 30% of the scattering coefficient. (Cabada et al. Submitted to Atmospheric Environment)

Meteorological influence on, and patterns in ambient fine particulate chemical composition at two sampling sites in metropolitan Pittsburgh: A 2001 intensive summer study.

The concentration and chemical composition of ambient fine particulate material (PM_{2.5}) is reported for two sampling sites in and near Pittsburgh, Pennsylvania: the Department of Energy National Energy Technology Laboratory (NETL) PM study site southeast of the city, and the Carnegie Mellon Pittsburgh Air Quality Study (PAQS) site 6 km east of central Pittsburgh established with funding by the EPA Supersites Program and by DOE-NETL. Data from these sampling sites were characterized by one to three-day episodes with PM_{2.5} concentrations (constructed from the sum of the chemical components) exceeding 40.0 µg/m³. The episodes were dominated by high concentrations of ammonium sulfate. The fine particle concentrations were compared with meteorological data from surface weather maps and a Hybrid Single Particle Lagrangian Integrated Trajectory model (HYSPLIT model), with back-trajectories estimated over 24 hours. High PM_{2.5} concentrations were associated with transition from a high pressure to a low pressure regime in advance of an approaching frontal system indicating longrange transport of pollutants. In contrast, fine particulate organic material appeared to be dominated by nearby sources. Distinct differences were observed in the diurnal variations in concentration between the two sites. The NETL site showed clear maximum concentrations of semi-volatile organic material (SVOM) during midday, and minimum concentrations of nonvolatile organic compounds in the afternoon. In contrast, the Carnegie Mellon PAQS site showed an absence of diurnal variation in SVOM, and minimum concentrations of nonvolatile organic compounds in the afternoon and evening. Neither site showed significant diurnal variation in ammonium sulfate. (Modey et al. Submitted to Atmospheric Environment)

Mass size distributions and size resolved chemical composition of fine particulate matter at the Pittsburgh Supersite

Size resolved aerosol mass and chemical composition were measured during the Pittsburgh Air Quality Study (PAQS). Daily samples were collected for 12 months from July 2001 to June 2002. Micro-orifice uniform deposit impactors (MOUDIs) were used to collect aerosol samples of fine particulate matter smaller than 10 µm. Measurements of PM_{0.056}, PM_{0.10}, PM_{0.18}, PM_{0.32}, PM_{0.56}, PM_{1.0}, PM_{1.8} and PM_{2.5} with the MOUDI are available for the full study period. Seasonal variations in the concentrations are observed for all size cuts. Higher concentrations are observed during the summer and lower during the winter.

Comparison between the PM_{2.5} measurements by the MOUDI and other integrated PM samplers reveals good agreement. Good correlation is observed for PM₁₀ between the MOUDI and an integrated sampler but the MOUDI underestimates PM₁₀ by 20%. Bouncing of particles from higher stages of the MOUDI (>PM_{2.5}) is not a major problem because of the low concentrations of coarse particles in the area. The main cause of coarse particle losses appears to be losses to the wall of the MOUDI.

Samples were collected on aluminum foils for analysis of carbonaceous material and on Teflon filters for analysis of particle mass and inorganic anions and cations. Daily samples were analyzed during the summer (July 2001) and the winter intensives (January 2002). During the summer around 50% of the organic material is lost from the aluminum foils as compared to a filter-based sampler. These losses are due to volatilization and bounce-off from the MOUDI stages. High nitrate losses from the MOUDI are also observed during the summer (above 70%). Good agreement between the gravimetrically determined mass and the sum of the masses of the individual compounds is obtained, if the lost mass from organics and the aerosol water content are included for the summer. For the winter no significant losses of material are detected and there exists reasonable agreement between the gravimetric mass and the sum of the concentrations of the individual compounds.

Ultrafine particles (below 100 nm) account for less than 5% of the PM_{2.5} mass, and show different composition for the summer and the winter intensive. During the summer the ultrafine mass is 50% carbonaceous material (organic material and elemental carbon) and 50% inorganic (mainly sulfate and ammonium); during the winter these percentages are 70% and 30% respectively. (Cabada et al. Submitted to Atmospheric Environment)

Semi-Continuous PM_{2.5} Inorganic Composition Measurements During The Pittsburgh Air Quality Study

A method for semi-continuous (10 minute time resolution) PM_{2.5} nitrate and sulfate measurements, based on the humidified impaction with flash volatilization design of Stolzenburg and Hering (2000), was evaluated at the Pittsburgh Air Quality Study Supersite from July 2001 to August 2002. The semi-continuous measurements were corrected for several operating parameters. These corrections resulted in an improvement in the agreement of the measurements with the filter-based measurements, with a major axis regression relationship of $y=0.83x+0.20 \text{ } \mu\text{g m}^{-3}$ and R^2 of 0.84 for nitrate and $y=0.71x+0.42 \text{ } \mu\text{g m}^{-3}$ and R^2 of 0.83 for sulfate. The corrected semi-continuous measurements were calibrated over the entire year using collocated filter-based measurements. These calibrated semi-continuous measurements are used in conjunction with temporally resolved gas phase measurements of total (gas and aerosol phase) nitrate and meteorological measurements to investigate short-term phenomena at the Pittsburgh Supersite. The gas-to-particle partitioning of nitrate varied daily and seasonally, with a majority of the nitrate in the particle phase at night and during the winter months. (Wittig et al. Submitted to Atmospheric Environment)

Mass Balance Closure and the Federal Reference Method for PM_{2.5} in Pittsburgh, Pennsylvania

Daily ambient aerosol samples were taken in Pittsburgh, Pennsylvania from the summer 2001 through winter 2002 as part of the Pittsburgh Air Quality Study (PAQS). The study measured PM_{2.5} mass by the Federal Reference Method (FRM) and the PM_{2.5} chemical composition by a variety of filter-based and continuous instruments. This paper examines the mass balance between the FRM measured mass and the sum of the aerosol

chemical components. For the seven month study period, the average FRM-measured mass is 11% greater than the sum of the mass of the aerosol chemical components. This mass balance discrepancy varies seasonally, with the average FRM-measured mass 17% greater than the sum of the chemical components for the summer months, with discrepancies as large as 30% during episodes. Meanwhile, the FRM-measured mass was at or slightly below the sum of the chemical components for the winter months.

The mass balance discrepancy and its seasonal shift cannot be explained by measurement uncertainty; instead the discrepancy is due to combination of retained aerosol water and volatilization losses. The relative importance of these different factors varies with aerosol composition and meteorology and causes the observed seasonal variation in the mass balance. The contribution of the aerosol water to the FRM measured mass is estimated using continuous measurements of aerosol water at the site; volatilization losses are estimated from other filter-based instruments. Water contributes 16% of the FRM mass in the summer, and 8% of the FRM mass in the winter; it appears responsible for episodes where the FRM-measured mass is significantly greater than the sum of components. Retention of water is greatest during acidic conditions, which commonly occur during the summer months. Volatilization losses are estimated at 5% of the FRM mass during the summer, and 9% for the winter. Volatilization losses appear to be most significant on days dominated by organic aerosol, or winter days with relatively high nitrate concentration. Accounting for the effects of water and volatilization losses close the mass balance between the FRM and the sum of the chemical components, providing insight into the FRM mass measurements. (Rees et al., Submitted to Atmospheric Environment).

Ambient Measurements of Metal-Containing PM 2.5 in an Urban Environment Using Laser-Induced Breakdown Spectroscopy

Laser-Induced Breakdown Spectroscopy (LIBS) was used to measure the distribution of seven species in individual ambient aerosol particles during an 8-day period from August 26 to September 2, 2002 at the Pittsburgh Aerosol Supersite. Particle hit rates were on the order of $10^{-4} - 10^{-5}$ for Al, Ca, Cr, Cu, Mg, Mn, and Na. Weekly average concentrations between 29 – 720 ng m⁻³ are reported along with conservative threshold detection limits for individual particles between 15 and 184 fg, depending on the element. Hourly concentrations are reported for Ca, Mg, and Na; Mg concentrations are found to be somewhat correlated with both Ca and Na, while Ca and Na appear uncorrelated. A representative example of measured Mg particle masses illustrates that the detection threshold poses a limitation in this data set, which could be rectified in future implementations. Finally, the presence of multi-element particles in the data set suggest the use of high-sensitivity, wide-range echelle spectrometers for particle source apportionment and determination of associations between elements. (Lithgow et al, Submitted to Atmospheric Environment)

CONCLUSIONS

Significant progress was made this project period on the source characterization, source apportionment, and deterministic modeling activities. Major accomplishments included: Development of an emission profile for an integrated coke production facility and simulations using PMCAMx for a two week period during July 2001. Initial comparisons with the data collected in Pittsburgh suggest good agreement between the model predictions and observations.

Work during the next project period will focus on the source apportionment and the deterministic modeling activities. We expect to have finalized the apportionment of the primary sources of organic aerosol for the July 2001 period. We also expect to have performed comparisons between PMCAMx predictions and a larger number of ambient sites including other supersites, and the EPA speciation trends network. We also will continue our efforts to identify a full-scale coal fired power plant for characterization.

PRESENTATIONS AND PUBLICATIONS

Publications:

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2. C. O. Stanier, A. Khlystov, and S. N. Pandis (2002) Chemical processes and long-range transport of aerosols: Insights from the Pittsburgh Air Quality Study, in *Long Range Transport of Air Pollution*, Kluwer.
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Presentations:

1. "Investigation of nucleation bursts in the Pittsburgh air quality study", 6th International Aerosol Conference, Taipei, Taiwan, September 2002 (C. O. Stanier, A. Y. Khlystov, and S. N. Pandis).
2. "Monitoring of water content of ambient aerosol during the Pittsburgh Air Quality Study" 6th International Aerosol Conference, Taipei, Taiwan, September 2002 (A. Y. Khlystov, C. O. Stanier, D. Vayenas, and S. N. Pandis).
3. Performance of the Aerodynamic Particle Sizer 3320 during the Pittsburgh Air Quality Study (PAQS)" 6th International Aerosol Conference, Taipei, Taiwan, September 2002 (A. Khlystov, C. Stanier, and S. N. Pandis).
4. "Sulfate-ammonia-nitric acid interactions in an urban area" 6th International Aerosol Conference, Taipei, Taiwan, September 2002 (S. Takahama, A. Khlystov, B. Wittig, S. V. Hering, C. Davidson, A. Robinson, and S. N. Pandis).
5. "Sampling artifacts during measurement of ambient carbonaceous aerosol" 6th International Aerosol Conference, Taipei, Taiwan, September 2002 (R. Subramanian, A. Y. Khlystov, J. C. Cabada, S. N. Pandis, and A. L. Robinson).

6. "Formation and properties of regional aerosol: Some insights from the Pittsburgh Air Quality Study", NASA-GSFC, Greenbelt MD, May 2002,(C. Stanier, A. Khlystov, S. Rees, J. Cabada, A. Robinson, C. Davidson, and S. N. Pandis)
7. "Seasonal composition of PM_{2.5} and performance of the Federal Reference Method in Pittsburgh", PM_{2.5} and Electric Power Generation, Pittsburgh, April 2002 (S. L. Rees, S. Takahama, A. L. Robinson, A. Khlystov, and S. N. Pandis).
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